IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

ATTY.'S DOCKET: MATSUI=5

In re Application of:	Art Unit: 1756
MATSUI et al.	Examiner: Martin J Angebranndt
Serial No.: 09/928,833	Washington, D.C.
Filed: August 14, 2001	January 12, 2006
For: OPTICAL RECORDING MEDIA	

DECLARATION UNDER 37 CFR 1.132

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Sir:

1. I am one of the coinventors in the captioned application.

2. I am a citizen of Japan residing at 2-18-102, Sayamadai 2-chome, 1-ban, Sayama-shi, Saitama 350-1304, Japan.

3. An accurate copy of my Curriculum Vitae was attached to the Declaration of June 8, 2005 which was filed to the United States Patent and Trademark Office on June 20, 2005.

4. Here I further state my opinion of JP60-204396 which has been cited as a prior art by the Examiner in the Official Action of August 22, 2005.

5. In my previous Declaration, I stated as follows:
The optical recording medium according to this invention is based on a recording strategy where in an optical medium using a violet or blue laser to effect recording and reading out of data, the laser is absorbed by a thin membrane of organic dye in the optical recording medium at a shorter wavelength region against the absorption maximum of the organic dye.

6. I carefully reviewed the whole content of JP60-204396 and concluded that the optical recording medium of this invention is still entirely novel against JP60-204396 and unobvious therefrom because JP60-204396 neither discloses nor suggests anything about

our recording strategy.

7. According to my knowledge and experience, JP60-204396 discloses at most a recording strategy which is feasible solely in optical recording media using a certain laser, for example, semiconductor laser, which gives an oscillation line around 750, 780 or 830 nm. JP60-204396 teaches in fact that data can be wrote in and read out from such an optical recording medium with the use of a laser whose wavelength lies within the range of 40 nm shorter to 70 nm longer than the absorption maximum wavelength of an organic dye. This recording strategy was however defined and tested only for semiconductor lasers with oscillation lines around 750, 780 or 830 nm (see line 8, right lower corner, page 15 to light upper corner, page 16 in JP60-203496). JP60-204396 is entirely silent on violet or blue laser per se, as well as disclosing or teaching nothing about the feasibility of such a recording strategy in optical recording media using violet or blue laser as light source. The reason must be that as well known in the art, violet or blue laser was at last brought into practical use in 1999, therefore unavailable at the time when JP60-204396 was filed.

8. JP60-204396 taught in fact that several lasers of He or Ar type, such as He-Ne, Ar and He-Cd lasers, could be used as light source in optical recording media. In the last Official Action, the Examiner stated that violet or blue laser may substitute for these lasers. According to my knowledge and experience, violet or blue laser never substitute for any lasers in JP60-204396 because of differences in oscillation wavelength and power. Each of He-Ne, Ar and He-Cd lasers give several distinct oscillation lines: For example, as well known in the art, Ar laser gives at least two oscillation lines around 488 and 515 nm. Each oscillation line however lies very far from violet or blue laser (usually around 400 nm), as well as from 750, 780 and 830 nm which were practically used in JP60-204396 to define and test its recording strategy.

9. As to optical recording media using a laser of Ar or He type, Kenryo Nanba, one of the coinventors in JP60-204396, later reported in "*Shikizai-Kogaku Handbook*" (Handbook of Colour Material Technology", page 1,272, edited by Japan Society of Colour Material, published by Asakura Shoten Publisher (1997) that in an earlier development stage of optical recording media, several distinct lasers of Ar or He type were in fact tried to

use as light source, as well as that such a trial was however proved to be unsuccessful because at that time, there were available no organic dyes which might give a sufficient reflection rate in optical recording media. As well known in the art, He-Cd laser gives much shorter oscillation lines (325 and 442 nm). If as reported by Nanba, organic dyes in an earlier development stage of optical recording media are less sensitive to Ar laser, then other shorter lasers such as those of He type would be much less practical in optical recording media.

10. Because of these facts, I do state again that according to the disclosure of JP60-204396, its recording strategy would be feasible only in optical recording media using a certain laser which gives an oscillation line around 750, 780 or 830 nm (for example, as in the case of CD-R), but unpractical in optical recording media where violet or blue laser, oscillation wavelength at around 400 nm, is used to write in or read out from optical recording media such as Blu-ray Disc and HD DVD-R.

11. I hereby further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon:

Fumio Matsui

Fumio MATSUI

12th day of January, 2006

Date

Excerpt Translation of "*Shikizai-Kogaku Handbook*" (Handbook of Colour Material Technology), edited by Japan Society of Colour Material, published by Asakura Shoten Publisher, 1997

色材工学
ハンドブック

(社)色材協会
編集

朝倉書店

6.　光記録材料

6.1　光記録材料の概要

今日の社会に氾濫する大量の情報を記憶しうるメモリーとして磁気記録媒体が使用されているが，より高密度，大容量化が必要となってきた．この要求を満たすために，追記型 (direct read after write; DRAW) または WO (write once)，WORM (write once read many) などと呼ばれる，ユーザーが記録再生可能な光メモリーディスクが 1981 年から市販されている[1]．当初は Te を主成分とする記録膜がほとんどであり，シアニン色素を用いた光メモリーディスクが 1985 年に実用化[2]されるにいたって，色素系記録膜の研究，開発が活発に進められている．このほか色素材料にはフォトクロミズムを示す物質などによるフォトンモード記録があり，消去，再記録可能な光メモリーの開発が期待されている（本編の 7.2 参照）．また，光の干渉を利用した記録方法としてホログラフィーがあるが，ここではヒートモード記録である追記型光記録用色素材料について述べる．

ヒートモード記録とは吸収した光エネルギーが熱エネルギーとなり，多くの Te 膜や色素膜が昇華，融解または分解して記録最小単位としてのピット（小孔）を形成する方法である．したがって，ピット形成時に物質移動をともなうため，ディスクは図 6.1 のようなエアーサンドイッチ構造をとり，膜面を自由とする必要がある．また，基板側からの反射率変化を信号として検出する記録再生方式がドライブに採用されていることから，記録膜には一定以上の反射率が要求される．開発の初期においては Ar や He-Ne レーザーなどの発振波長に吸収をもつ，反射率の低い色素が用いられていたために，金属反射膜を設けることが必要であり，実用にはなっていない[3]．

半導体レーザーの発振波長（近赤外）に吸収を示す色素の探索が進められ，バナジルフタロシアニンの単層膜が吸収と同時に高い反射率を示すことが報告された[4]が，低感度であり，また蒸着膜であったことから，色素材料を用いた光メモリーディスクの特徴が生かされなかった．

色素系追記型光メモリーディスクの主な特徴は，長所として長寿命，低毒性，製膜工程の低コスト化（スピンコート法），高感度，などがあげられる．短所としては，低反射率，記録閾値が不明確，再生光に対してヒートモードの劣化，また再生光および環境光に対してフォトンモードの劣化などを起こす場合がある[5,6]．ただし，環境光に対しては，ディスクがケース入りとなった[7]ためにほとんど問題ないとされている．

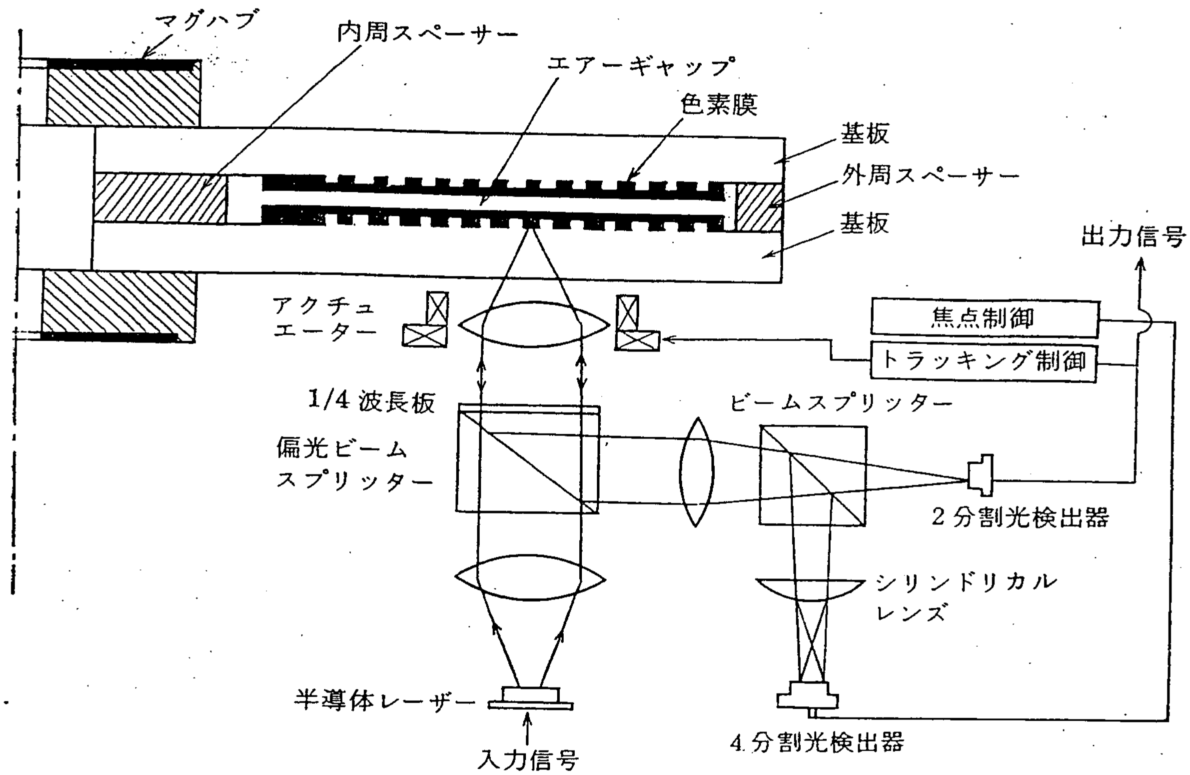

図 6.1 有機色素系光ディスクの基本構成
エアーサンドイッチ構造はピット形成型の追記型光ディスクに共通のもの.
光学ヘッドからの光は基板を通して記録再生を行う.

6.2 光メモリーディスク用色素に要求される特性

色素を用いた光メモリーディスクの長所および特に短所を考慮すれば，光メモリーディスク用色素に必要とされる特性は，以下のようになる[6].

(1) 薄膜化できること．特に，スピンコート法で製膜するためには適当な溶剤に可溶であること．溶剤は適度な比蒸発速度をもち，ポリカーボネート基板を侵さないマイルドなものが望ましい．

(2) 薄膜は均一であって，結晶化など粒子性を示さないこと．

(3) 薄膜は記録再生用レーザーの発振波長において，十分な吸収をもつこと．

(4) 吸収と同時に，同一波長において適度な反射率をもっていること．

(5) 吸収および反射の波長依存性はなるべく小さく，レーザー発振波長付近でなるべくブロードであること．

(6) 融点，熱分解点，昇華点などが適当な温度であり，なるべく急激に変化すること．

(7) 熱，光，湿気その他のガスに対して安定であること．

(8) 毒性のないこと．

最近，以上の要求特性を備えた光メモリー用色素の提案が急増しているが，多くは古くから知られている色素骨格を分子設計し直したもの，または電子写真用感光体として開発され

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<u>Translation of page 1,272, 2nd paragraph</u>

"Heat mode recording system is a method where pits (small pores), as minimum recording units, are formed in such a manner of converting absorbed light energy into heat energy and then subliming, melting or decomposing most of the Te (tellurium) membranes or dyes used in organic dye optical recording media. Therefore, heat mode recording system accompanies the transfer of substances when pits are formed, and discs for organic dye optical recording media should have the air-sandwich structure as shown in FIG. 6.1 and the surface of the discs should be made to allow the substances to move freely. The organic dye optical recording media employ in a drive unit a recording and reading out system for detecting as signals a reflection change in substrates so that recording membranes are required to have a prescribed level of reflectance. In the beginning of exploitation, no organic dye optical recording medium was succeeded in actual use because such optical recording medium inevitably required a metallic reflection membrane due to the use of dyes which had a relatively low reflectance and an absorption at the oscillation wavelength of Argon or HeNe laser."

<u>Translation of page 1,273, FIG. 6.1</u>

6. Optical recording material

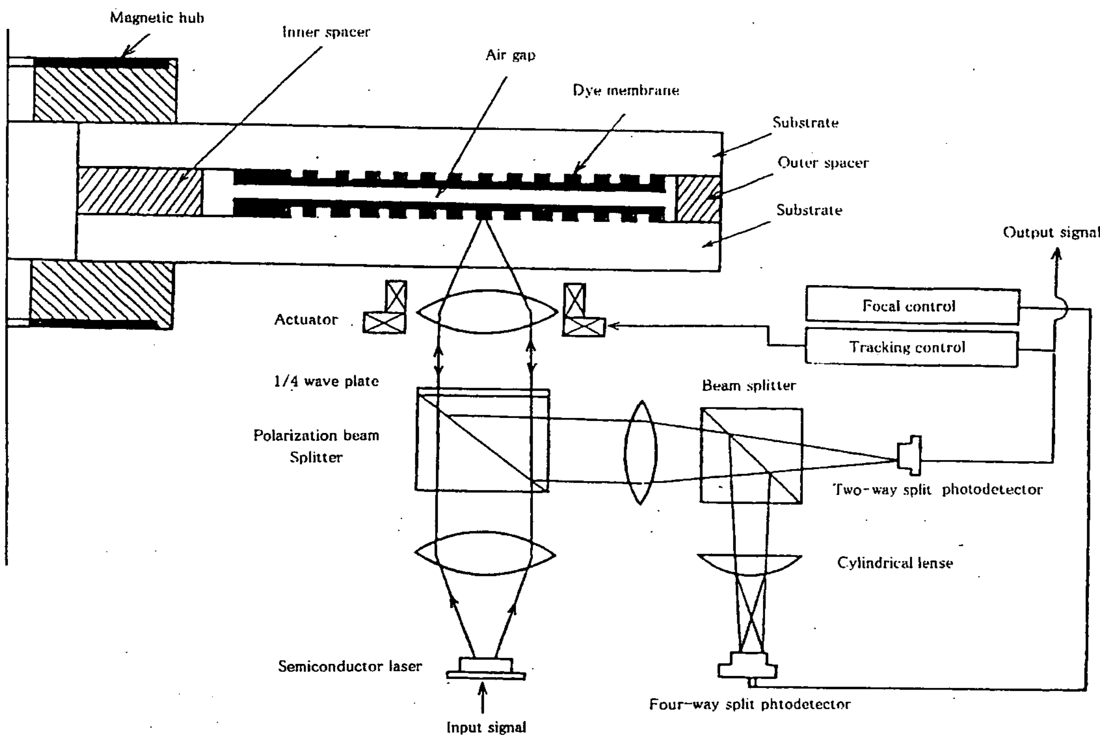

FIG. 6.1 Basic structure of organic dye optical disc
Air-sandwitch structure is a common structure in write-once optical disc in a pit-formation type.
Light passing through optical head records/writes information.

MAGNETO-OPTICAL RECORDING MATERIALS

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CONTENTS

Chapter 1 INTRODUCTION

Takao Suzuki

1.1 INTRODUCTION

Today, electronic information is pervasive: text, digital audio and video, graphics, telecommunication and so on, and various information-storage technologies have been developed in the past decade. Among them, optical storage is rather a newcomer, though its unique features and advantages in the storage industry have been known for a long time. With significant developments in the laser and semiconductor industries, optical storage technology has already successfully emerged into the consumer market and more recently into the computer-based data storage market as well.

The 120 mm, prerecorded compact disc (CD), having the standard format specified in the Red Book[1] and the rewritable 5¼″ and 3.5″ size magneto-optical (M-O) technologies are noteworthy. While it took more than seven years for the CD market to take off, it is now a very prosperous industry, with over 500 million disks produced in 1996 vs. 200 million in 1993. For computer-based data storage and multifunctional purposes, the first generation of the ISO[2] standard 5¼″ M-O drive (325 MB × 2/double-sided) was introduced in 1988 and the 3.5″ drive (128 MB) in 1991. Since then, progress has been remarkable in capacity and data transfer rate as well as cost performance, and the so-called 2X (650 MB × 2/5¼″ double-sided disk) and 3X (1 GB × 2/5¼″ double-sided disk) drives are now in the market. Also, a remarkable product called the MiniDisc (2.5″), which was the first recordable optical system for both the consumer and the data market, has made a breakthrough in the technology utilizing data compression and direct overwrite schemes. Furthermore, archival storage has become, for legal reasons, a more necessary requirement of various financial, medical, and telecommunication industries as well as government agencies, where terabytes of storage (10^{12} bytes) are not atypical. In this application area, various types of write-once/read-many (WORM) optical libraries have been developed, where their permanent form of storage is being well accepted in the marketplace.

Many types of optical storage media have been intensively studied for various applications. Figure 1.1 illustrates some examples. Except for the magneto-optical recording medium, the optical contrast (signal) results from the reflectivity difference between the written and unwritten marks. For magneto-optical recording media, a

[1]The physical standards for CD Audio were originally published in a red binder and have become known as the Red Book. Subsequent standards have been called the Yellow Book for CD-Read-only Memory (CD-ROM), the Green Book, Orange Book, etc. (see Table 1.1, and also Chapt. 11).

[2]ISO stands for International Standards Organization. The file format for the CD-ROM is defined in Standard ISO 9660.

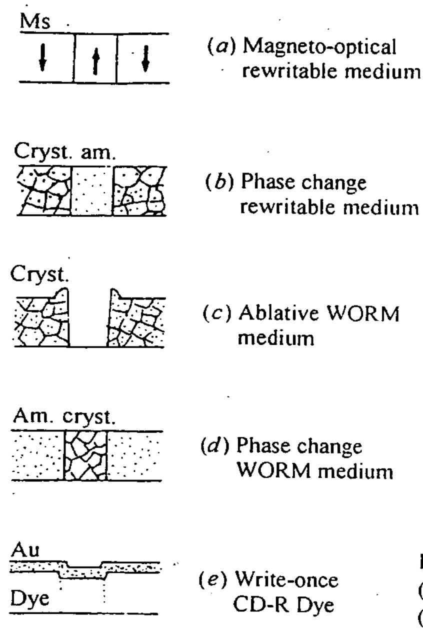

Figure 1.1 Various types of optical media: (*a*) and (*b*) are rewritable media, (*c*) through (*e*) are the writable media.

change in polarization direction due to the magnetization direction is the source of the contrast.

Key features of optical storage technology are removability and high capacity on a disk. The removability is important because it allows access to multifunctional applications with compatibility from drive to drive. It also allows us to transport huge amounts of information by hand. For example, one can carry the information equivalent to a 40,000-page document (2 ft high) in an optical 5 ¼″ disk. Capacity is important because it translates to low cost/MB and to space-efficient storage. The latter is important especially for places such as Japan where land/office prices are anomalously high. Consider, for instance, an insurance company that desperately needs to rid itself of paper claim forms—but needs access to customers' records instantly. Scanning these original documents and storing them on magnetic hard disk drives would be too costly, while tape systems would not have enough speed to randomly retrieve hundreds of thousands of images in a timely manner. Optical storage provides the best solution for this dilemma. Figure 1.2 shows the progress of optical disk storage technology under 12″ size. The increase in capacity is more than 50% per year in the past six years.

While optical storage is an attractive storage technology, magnetic hard disk recording is the dominant technology for information storage. Its growth rate in density has been almost 30% per year for the past 40 years. In the past couple of years, the increase is close to 60% and is expected to continue on the increased capacity rate well into the foreseeable future. Driven by such an ongoing increase in storage densities of magnetic recording, and confronted by upcoming multimedia applications which demand more user data capacity, substantial efforts have been focused on the improvement of storage density (and data transfer rate) in optical storage systems as well.

By no means is the solution for increasing the capacity simple since such an increase must be decided by such factors as backward compatibility. This feature is important to removable media because the customer expects new products to be com-

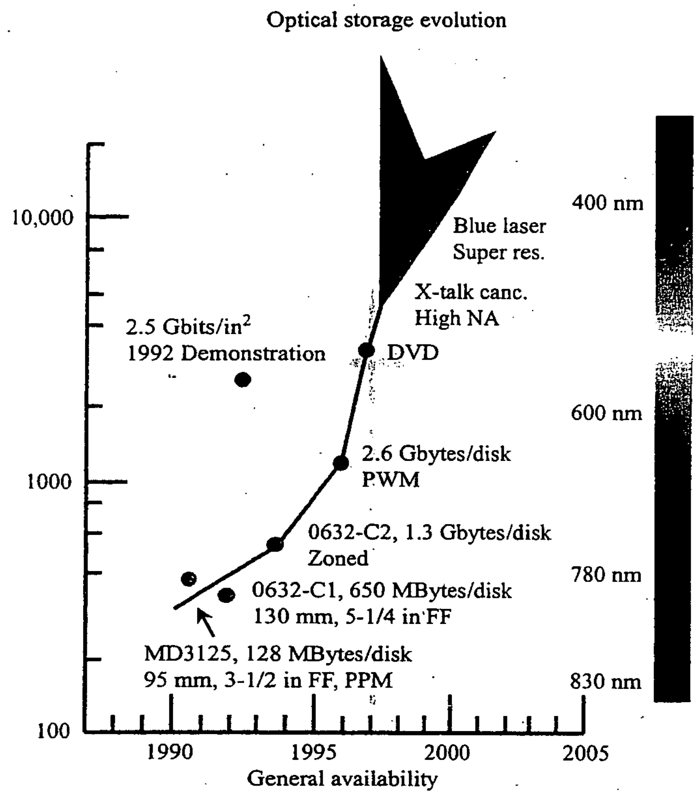

Figure 1.2 Evolution of optical storage technology. The acronyms are explained in the text.

patible with their previous investments in data stored on older generation media. Another key factor is cost. The sale price ($/MB) must be significantly lower compared to other prior generations of optical storage products and alternative storage systems (e.g., removable hard disk drives).

To increase the capacity in optical storage media, many solutions are possible:

Shorter wavelengths [1],

$$1.5(670\,\text{nm}) \sim 3.8\text{X}(428\,\text{nm})$$

Magnetically induced super resolution (MSR) [2, 3]
(see Chapter 9)

$$\geq 2\text{X}$$

Pulse width modulation (PWM)

$$1.5 \sim 2\text{X}$$

PAPERS

Organic colorants for laser disc optical data storage

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INTRODUCTION

Many functional dyes and pigments are widely used in electronics, utilising the traditional properties of dyes and pigments as used for textile coloration. In Japan we named them *Kinouseisikiso* (functional colorants or dyes) in 1980 to distinguish them clearly from dyes for colouring textiles [1–5].

Research into optical data storage began at Stanford University [6], and Compaan et al. of Philips developed a video system using a laser as early as 1972 incorporating this technology [7]. With the mass production of the laser diode, which is a light source for writing and reading in the optical disc system, new audio appliances such as CD (compact disc) and LD (laser disc) systems using the optical disc memory have been developed. In the future the optical disc memory will be an increasingly important system of data storage, replacing the magnetic disc memory. The main features of the optical disc are as follows [8]:

(a) High density and capacity for the recording (1 giga byte for a 20 cm disc, equivalent to approximately 10^4 sheets of A4 paper)
(b) Fast access time for reading (0.2 s)
(c) Dust and scratches on the disc surface have little effect on recording and reading, as the laser pick-up does not come into contact with the recorded surface.

There are three kinds of optical discs. The first is used only for reading information which has been already recorded, called a ROM disc, e.g. the CD or LD. The second is also for reading but also offers the facility to make one recording, called the DRAW disc or write-one disc. The third type permits rewriting, called the erasable disc or rewrite disc, analogous to conventional video or audio tape. A lot of ROM discs, such as the CD, are already on the market at present, and a few of the other types are also available commercially. Research into the DRAW (direct reading after writing mode) disc is continuing, the first system using it being developed by Philips in 1978 [9]. Recently in Japan the DRAW disc using Te-Ox (tellurium oxides) colorants has been introduced, and at present work to introduce organic colorants into DRAW disc technology is being actively pursued.

In this paper the application of organic colorants to optical disc memory in the heat-mode system will be described after first outlining the basic principle of the optical disc memory in this system.

Principles of the optical DRAW disc memory

There are two main types of optical DRAW disc memory. The first is called the heat-mode system. In this system microscopic pits in the coloured recording layer of a disc are formed by thermal energy transformed from the photo energy of a laser. The second involves a change of properties of the substrate in the disc, e.g. refractive index or reflectivity, caused by laser irradiation.

Organic colorants are particularly important in the heat-mode system. The principle in this mode is shown in Figure 1. There are two kinds of heat-mode discs. The first is a mono-layer type and the second is a bi- or tri-layer type, which mainly consists of the recording layer, the reflecting layer and the substrate, although in the latter type it is difficult to form the necessary thin multiple layers. The former type, as shown in Figure 1, consists of a plastic substrate such as transparent polycarbonate (PC) or polymethylmethacrylate (PMMA) and a recording layer containing colorants formed by sputtering, vacuum evaporation or spin-coating techniques. The thickness of the recording layer is approximately 30–100 nm.

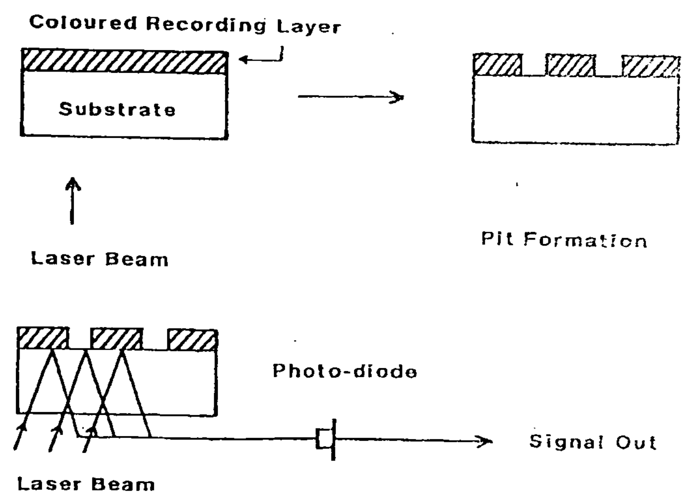


Figure 1 – Principle of the mono-layer type of DRAW disc

The recording (writing) process on a DRAW disc is achieved as follows. A pit (diameter 1 μm) in the recording layer is formed by a laser beam from the laser diode with a power of 20–30 mW. The diameter of the pit is approximately the same as that of the spot formed by the laser beam.

In the reproducing (reading) process the presence of pits is detected by differences in reflectivity using a laser beam of weak power (approx. one-tenth of that for recording), and the signal is picked up by a photo-diode for subsequent reproduction. The laser diode plays an important role in this type of optical data storage.

Laser diodes for optical disc memory

There are two kinds of laser, gas lasers such as the Ar^+ laser or the $He–Ne^+$ laser, and laser diodes that can be used for optical data storage. The gas lasers utilise oscillation wavelengths in the visible range (450–680 nm), as shown in Table 1; this is a single oscillation, which is not tunable and it is difficult to miniaturise the oscillators. On the other hand laser diodes are small devices which can be attached to various types of apparatus, the oscillation wavelengths being in the near-infra-red region and tunable.

TABLE 1

Main oscillation wavelengths of gas lasers in the visible region

Gas laser	Oscillation wavelength (nm)			
Ar^+	457.9	476.5	488.0	496.5
	501.7	514.5		
$He–Ne^+$	632.8			
$Kr^{+(a)}$	476.2	482.5	520.8	530.9
	568.2	647.7	676.4	

(a) Oscillation wavelengths in the near infra-red region (752.5, 793.1 and 799.3 nm) are also present

The laser diodes are of two basic types: gallium–arsenic (Ga–As) and indium–phosphorus (In–P) (in Al–Ga–As laser diodes the substrate is Ga–As, and in In–Ga–As–P laser diodes the substrate is In–P [4]). Their oscillation wavelengths are 780–840 nm and 1200–1600 nm respectively. At present the Ga–As laser diode is the most widely used source for optical data storage, while the In–P laser diode is used principally as a source for communications using optical fibres.

Holonyak et al. were the first to succeed in generating a pulse oscillation at 710 nm using a Ga–As–P device at 77 K [10]. Many researchers during the period 1976–80 also achieved a continuous oscillation at 710 nm using various laser diodes at room temperature [11]. Theoretically the lower limit of the oscillation wavelength is about 660 nm, and recently it has been reported that oscillation at 661.7 nm [12] (or 583.6 nm [13] using a Al–Ga–In–P laser diode) has been accomplished at room temperature.

The shorter the wavelength of the laser beam used for recording, the higher is the density and sensitivity of the recording process, since the diameter of the laser spot is proportional to the oscillation wavelength of the laser diode, as expressed by the empirical Eqn 1 [4]:

$$R_0=\frac{k\lambda}{N_a} \qquad (1)$$

where R_0 = diameter of laser spot
k = constant (1.22 or 0.52)
λ = wavelength of laser
N_a = numerical aperture.

However, development of commercially available laser diodes with oscillation wavelengths below 700 nm is technologically very difficult, as the laser diode for the DRAW disc needs a high power at room temperature (at present 20–40 mW, in future 100 mW).

The Ga–As laser diode is manufactured in high quantities at low price, since the MOCVD (metal organic chemical vapour deposition) method [14] has been industrially established since 1984 [4]. The development of laser diodes with shorter oscillation wavelengths is expected for higher density recording; however, the main oscillation wavelength of commercially available laser diodes is still restricted to the 780 nm of a Ga–As laser. For this reason organic colorants in the recording layer of the DRAW disc need to have an absorption band in the near-infra-red region (780–840 nm) at present.

ORGANIC COLORANTS FOR THE DRAW DISC

The use of organic colorants instead of inorganic colorants such as Te-Ox in a recording layer of the optical disc offers the following practical advantages:

(a) Lowering of manufacturing cost of the optical disc
(b) High recording density
(c) Low toxicity
(d) Easy modification to improve disc characteristics.

For use in a DRAW disc organic colorants need to have an absorption band in the near-infra-red region, if a Ga–As laser diode is used as the laser source. The absorbed photo energy must be transformed into thermal energy. The values of molar absorptivity (ϵ) need to be large ($>10^4$) as the recording sensitivity depends on ϵ.

The dyes must also reflect the laser beam, as in the reproducing process pits are detected by differences in reflectivity, the reflectivity qualitatively increasing with increasing absorbance. The maximum wavelength of reflectance is slightly shifted to a longer wavelength than that of absorbance in a polymer film coloured by an organic dye [15], as shown in Figure 2. In practice the reflectivity of a mono-layer disc needs to be above 20% in order to give an acceptable signal-to-noise ratio.

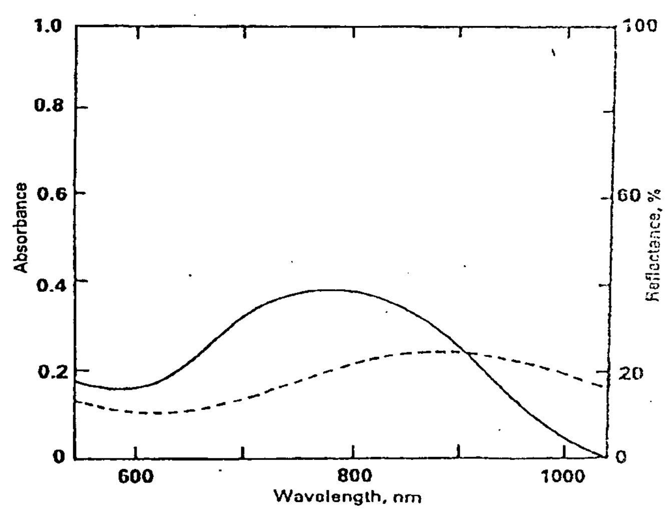


Figure 2 – Reflectance (dashed line) and absorbance (solid line) spectra of a film coloured by an organic dye with absorbance in the near-infra-red region

Another necessary property of organic colorants for this application is that they should be capable of being sublimed, when the recording layer is formed by a vacuum evaporation technique. Alternatively they need good solubility in appropriate organic solvents when the recording layer is formed by the spin-coating technique. The solubility parameter is very important at present, as the coating technique is mainly used to keep down the manufacturing costs of optical discs.

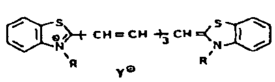
Finally the light fastness of the dyes must be good, as a recorded disc has to have a working life of ten years or more. The photofading of organic colorants by a laser beam in the reproducing process has to be minimised.

Triphenylmethane dyes [16], fluorescein (C.I. Acid Yellow 73) [17], and a polyester yellow [18] having good absorption in the visible region were first used as colorants in this area, as the first lasers had oscillation wavelengths in the visible region. Nowadays colorants having absorption in the near-infra-red region have become more important as the use of laser diodes has grown. Organic colorants used for the DRAW disc are described below.

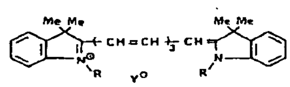
Cyanine dyes

The absorption maxima of cyanine dyes undergo a bathochromic shift as the number of vinylene groups increases, and indeed can be shifted into the near-infra-red region. PPP molecular orbital calculations give remarkably good predictions of the absorption band for cyanine dyes [19,20].

Typical cyanine dyes used for the DRAW disc are shown in Figure 3; compounds 1 and 2 containing benzothiazoles or indoles as terminal heterocyclic rings [21,22] are widely used, although compounds 3 and 4 are also known [3,23,24]. Cyanine dyes containing quinolines or benzoxazoles as heterocyclic rings [3,25,26] have been mentioned in patents.

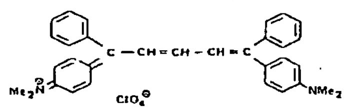


Compound 1

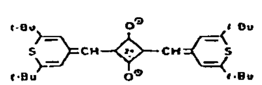


Compound 2

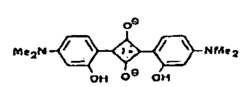
Compound 3



Compound 4



Compound 5



Compound 6

R = Me, Et
n = 1 or 2
Y = I^-, ClO_4^-
X = O, NEt, S, Se, Te

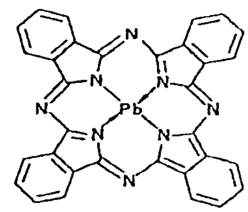
Figure 3 – Cyanine dyes used in laser disc optical data storage

These colorants have large absorption maxima at approximately 800 nm. Their reflectivity (>30%) makes them suitable for use in the DRAW disc. The photo-oxidation of cyanine dyes by a laser is improved by introducing a cyclic unsaturated group, carbonyl group or hetero atom in the centre of the polyalkene, as the linear conjugation in cyanine dyes is broken by photo-oxidation [3]. Photo-oxidation of cyanine dyes is also promoted by addition of metal complexes, as described below.

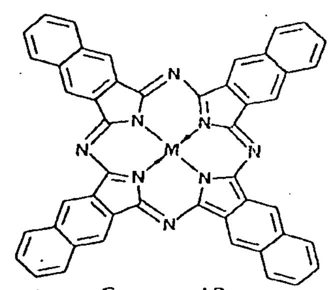
Squarylium dyes can also be regarded as cyanine dyes. The wavelength of maximum absorbance of squarylium dyes is shifted to a longer wavelength, by some 20–60 nm, than that of the corresponding cyanine dyes. The solubility of squarylium dyes in organic solvents is generally poor, but can be improved by introducing t-butyl or hydroxy groups, as in compounds 5 and 6 (Figure 3). The DRAW disc using compounds 5 or 6 can be formed by a coating technique, with high reflectivity (>20%) at 800 nm and good recording properties [24,27].

Phthalocyanine colorants

Phthalocyanine compounds were investigated from an early stage as colorants for optical data storage. The absorption maximum of free-base phthalocyanine is 686 nm [20], but lead phthalocyanine (Figure 4, compound 7) and titanyl or vanadyl phthalocyanine [5,28] have absorption maxima at approximately 800 nm and can be sublimed. Thus thin coloured layers can be formed using these phthalocyanines by means of a vacuum evaporation technique. Recently the naphthalocyanine compound 8 (Figure 4), obtained by replacing the benzene rings of the appropriate phthalocyanine structure with naphthalene rings, has been used in a DRAW disc [29].



Compound 7



Compound 8

M = Al, Ti

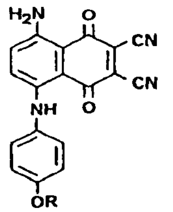
Figure 4 – Phthalocyanine colorants used in laser disc optical data storage

The solubility of phthalocyanine colorants in organic solvents is generally poor but is improved by introducing alkyl groups with long chains. The structure of crystals of phthalocyanine colorants changes readily by exposure to heat, light or solvents, and these influence the recording properties of the optical disc [30]. Tetradehydrocholine, which is stable to heat and light, has been mentioned in patents as a colorant for the optical disc [31].

Naphthoquinone dyes

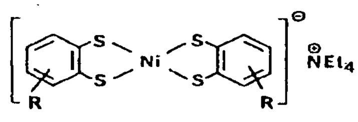
Naphthoquinone dyes that absorb in the near-infra-red region were first prepared by Griffiths et al. in 1978 [32].

They are obtained by a suitable combination of the donor substituent and a powerful acceptor substituent in 1,4-naphthoquinone, as shown in Figure 5 (compound 9). They have been developed for use as colorants for the DRAW disc by Esho et al. [33], and they confer high reflectivity (>30%) and good light fastness to the optical disc. Anthraquinone dyes absorbing in the near-infra-red region are also prepared by a similar reaction with 1,4-naphthoquinone [34]. PPP molecular orbital calculations predict accurately the absorption maxima in the near-infra-red region of these dyes, as they do with cyanine dyes.

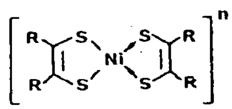


R = Et, n-Bu

Compound 9



Compound 10



Compound 11

n = 0,-1 R = aryl, alkyl

Figure 5 – Naphthoquinonoid dyes and dithiolate nickel complexes used in laser disc optical data storage

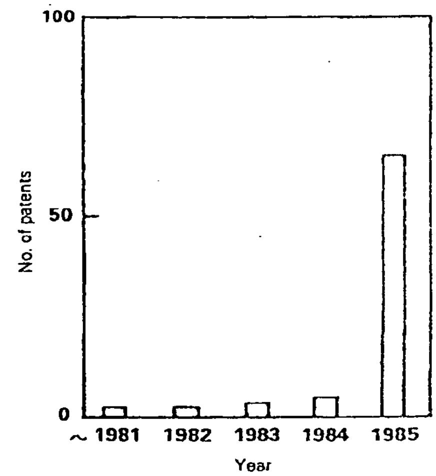


Figure 6 – Number of patents mentioning dithiolate nickel and related complexes used in optical discs (information compiled from Chemical Abstracts*)*

Dithiolate nickel complexes

Dithiolate nickel complexes 10 and 11 (Figure 5) [35,36] have absorption bands in the near-infra-red region (800–950 nm), but the absorption band in PMMA and PC is shifted to a longer wavelength (by 20–60 nm) than the oscillation wavelength of the Ga–As laser diode. Their solubility in organic solvents is poor and they confer low reflectivity.

The dithiolate nickel complexes are known as quenchers of singlet oxygen, dyes for lasers, catalysts and infra-red absorbers in sunglasses or goggles, and furthermore they are already widely used as important antioxidants for plastics [37]. They are applied to the coloured layer of the DRAW disc together with cyanine dyes as antioxidants. The number of patents in which these nickel complexes are featured has increased recently, as shown in Figure 6. Although these complexes are necessary to protect the coloured layer of the DRAW disc from photo-oxidation, the detailed mechanisms of photofading in the optical disc are as yet unknown.

Other colorants

New phenothiazinequinones from 1,4-naphthoquinones and anthraquinones [38–40], indonaphthols [41], thiapyrylium salts [42], azo dyes [43] and triphenylmethane dyes [44] have been prepared as colorants that absorb in the near-infra-red region. In the near future, if the development of laser diodes with oscillation wavelengths of 670–680 nm is successful, new colorants absorbing in this region will also be necessary.

A list of organic colorants, recording features and companies involved in DRAW disc technology at present, is given in Table 2 [3].

TABLE 2

Characteristics of the DRAW disc using organic colorants

Colorant	Recording properties[(a)]	Developer	Ref.
Cyanine dye 4 or squarylium dye 5	799 nm Kr^+ laser, 30 mJ/cm^2 SN≥ 45 dB	Philips	[24]
Naphthoquinone dye 9	830 nm LD, 11.5 mW SN≥ 50 dB	NEC	[33]
Organic dyes	830 nm, LD, >7 mW SN≥45 dB	Kodak	[45]
Cyanine dye 2[(b)] and nickel complex 10	790 nm LD, 3.2 mW SN≥ 58 dB	Ricoh	[22]

(a) SN – signal-to-noise ratio, LD – laser diode
(b) Several patents for the DRAW disc involving cyanine dyes and nickel complexes have also been published by TDK [46]

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Dyeing properties of monoazo disperse dyes derived from 4-alkylamidosalicylic acids: equilibrium study

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The dyeing equilibria of a set of monoazo dyes derived from 4-alkylamidosalicylic acids on nylon 6.6 have been studied. A Nernst distribution has been obtained indicating the prevailing mechanism of solution of the dye in the fibre. Equilibrium depends on the length of the alkyl chain of the dye and on the concentration of dispersant. The latter affects the equilibrium differently according to the hydrophobicity of the dye. Linear relationships between the chain length and ΔH° and ΔS° have been found.

INTRODUCTION

A series of 65 azo dyes derived from 4-alkylamidosalicylic acids have previously been described [1]. These dyes have the general structure shown in Figure 1, in which X_1, X_2 and X_3 are usual substituents and R is a C_1–C_{15} linear alkyl chain. The dyes have been used for the dyeing of nylon 6.6 fabrics, and their technical properties (fastness to light, alkali, perspiration and washing) were tested and quantitatively correlated to the structure using the SIMCA–PLS method [2].

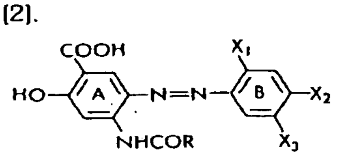
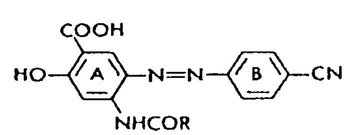


Figure 1 – Dyes used in previous study

In this paper we report the preliminary results of an extensive investigation based on the quantitative evaluation of the dyeing behaviour of dyes having the general structure shown in Figure 2. The substitution in the B ring was limited to one cyano group (chosen on the basis of properties previously observed [1], as the major aim of our work was the study of the effect of the chain length. The compounds, with their highly hydrophobic nature, were used as disperse dyes for the dyeing of nylon 6.6 fibres.



R = CH_3, C_3H_7, C_7H_{15}, $C_{11}H_{23}$, $C_{15}H_{31}$

Figure 2 – Dyes used in the present study

The structure of the dyes poses a problem about the nature of the mechanism of dye–substrate interaction. If dyes behave as dispersions, a Nernst linear isotherm should be observed as a consequence of the solution of the dyes into the fibre and of the low-energy chemical bonding, dispersion and dipole–dipole forces [3]. If the carboxyl group plays a relevant part in the dyeing mechanism, the dyes behave as acid dyes and the dyeing should be governed by a Langmuir isotherm, mainly connected with ionic interactions between dye anions and

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Development of Organic Recording Media for Blue-High NA Optical Disc System

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INTRODUCTION

Dissimilar to CD and DVD format, the next generation optical disc format, DVR-Blue[1)], will employ phase change material. This implies that the write once media compatible to such format will be designed to possess relatively low initial reflectivity compared to CD-R or DVD-R, and thus a reflective metal layer is no longer necessary. Readout principle in this case is based on a direct reflectivity modulation, enabling full compatibility with phase change material. Such new concept for organic recordable media is recently proposed and demonstrated using land/groove substrate[2)]. Further optimisation of the media on the most updated DVR-Blue compatible substrate is shown in this report, with an analysis on optical property and recording mechanism of the organic recording material.

EXPERIMENTAL SETUP

Recording experiment was carried out with a pulstec DDU-1000 player which comprises of NA = 0.85 objective lens and 404 nm wavelength laser diode as an optical pickup. Substrate used was almost identical to that of phase change media; track pitch was 0.32 μm with its groove depth of 20 nm, and the recording was made on the groove surface closer to the objective lens. Linear recording density was 0.13 μm/bit using (1,7) RLL modulation, which corresponds to 21.5 GB per single side 12 cm diameter disc. The recording and readout experiment were performed under linear velocity at 5.72 m/s.

Organic recording medium was improved to possess as high a refractive index (n) as possible, achieving n = 2.58 with appropriate absorption coefficient (k) of 0.31. To obtain a maximum reflectivity without any additional optical enhancement layer, the layer structure employed in this experiment was

PC substrate / Organic recording material (40 nm) / SiO_2 (25 nm) / PC sheet with PSA (0.1 mm),

where PC and PSA represents a polycarbonate and a pressure sensitive adhesive, respectively. The buffer SiO_2 layer between recording layer and PSA was deposited by reactive RF sputtering under $Ar+O_2$ atmosphere. The recording

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layer was evaporated at a temperature range of 210-260°C. Measured reflectivity of obtained media at 404 nm wavelength before the recording was 18%.

SINGLE CARRIER RECORDING AND READOUT

To clarify a basic recording and readout characteristics of the media, a single carrier recording with largest mark (8T, 0.693 μm) is performed. The recording pulse strategy was identical to that of DVD-R. Peak power of the recording pulse train was varied in Fig. 1 to show its recording sensitivity and modulation amplitude. Readout power was set as 0.3 mW. As a result, carrier-to-noise ratio (C/N) reached 55 dB at the maximum recording power, with its amplitude close to 50%.

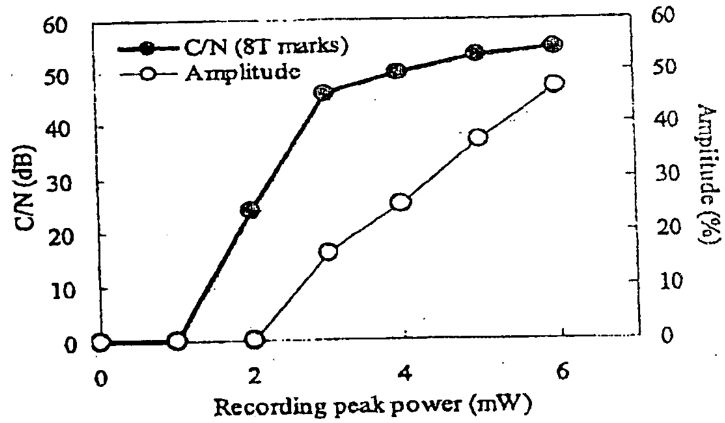

Fig. 1. Single carrier recording on an organic recordable media using DVR-Blue pickup. Maximum C/N for 0.693 μm mark was 55 dB, with 47% modulation amplitude.

For the smallest mark (2T, 0.173 μm), however, the optimum recording power was about 5 mW taking account its biasing balance between the 8T marks. The C/N was 43.5 dB under this condition. Since the noise level was shot noise limited, readout power was increased to enhance the C/N at this frequency. By applying 0.5 mW of readout power, C/N improved to 46.7 dB. Even under such high readout power, the readout signal were astonishingly stable; no decrease of C/N were observed after several hours of continuous readout on an identical track.

RECORDING MECHANISM

In order to analyse the recording mechanism, 8T single carrier recorded area by 6 mW peak power was observed with a spectral microscope (Zeiss UMSP 80). The image was observed using NA~0.20 lens from PC sheet side as a transmission of a Xe-lamp. Since the recorded marks were 50% duty against spaces, also taking account the unrecorded grooved area, absorption spectrum from the recorded area are de-convoluted by 45% from the spectrum of unrecorded area and converted to k value as shown in Fig. 2. A clear reduction of the

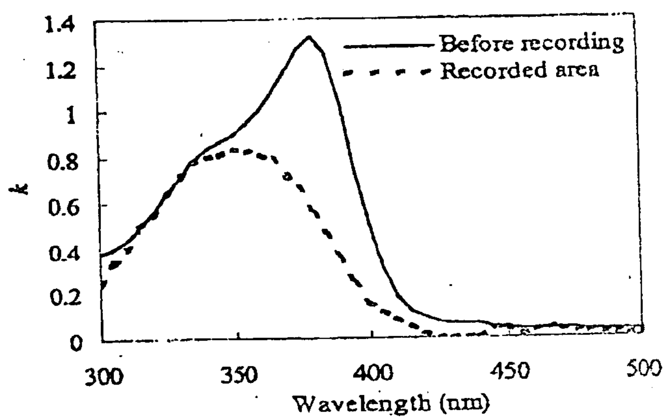

Fig. 2. Absorption spectra of the media. Recorded spectrum represents the area inside the 8T mark, extracted from multi-track single carrier recorded area.

absorption is observed after the recording, especially the peak at 380 nm.

From a Kramers-Kronig relation between n and k, the n value at 404 nm after the recording was estimated from Fig. 2. The result was n = 2.15, which will lead to the reflectivity of 9%. This matches very well to the readout experiment which showed modulation amplitude of 47%. It is evident from these data that the recording mechanism is mostly owing to the optical constant change of the organic material.

RANDOM PATTERN RECORDING

A (1,7) RLL modulation random pattern recording was made on the media with peak power of 5 mW and read out with 0.5 mW power. Shown in Fig. 3 is an equalizer passed eye-pattern after a single track recording, under linear density of 0.13 μm/bit. The jitter level was 8.5%. A continuous multi-track recording, which is the actual usage of a write once media, was also performed. Resulting jitter level achieved 10%, reaching a practical level for commercial use. Since the modulation is not yet saturated at this recording power as it is seen in Fig. 1, this media shows its high potential for further improvement, by optimisation of the recording pulse strategy and the recording material.

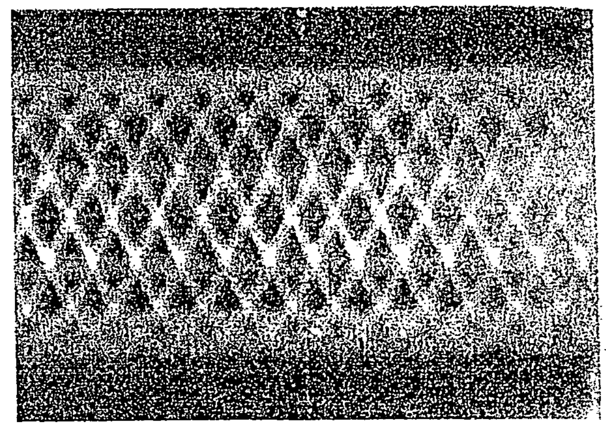

Fig. 3. Eye-pattern of the organic write once media with (1,7) RLL modulation. Recording density was 0.13 μm/bit and track pitch of 0.32 μm which corresponds to 21.5 GB/12 cm diameter disc. A single track recorded area were read out through a normal equalizer, resulting with jitter level of 8.5%.

CONCLUSION

We have developed an organic write once media suitable for DVR-Blue format. By use of organic material with high initial refractive index at 404 nm wavelength, a high density recording of 21 GB per 12 cm diameter single side disc was optimised to a practical level. Further optimisation of the recording pulse strategy and the media in near future promises the achievement of full compatibility to DVR-Blue format.

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